16 Lumen Modifications

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CONTENTS

16.1 METHODS

16.1.1 *IN SITU* POLYMERIZATION OF LIQUID MONOMERS IN THE LUMENS

When wood is vacuum impregnated with liquid vinyl monomers that do not swell wood, and then *in situ* polymerized either by chemical catalyst-heat, or gamma radiation, the polymer is located almost solely in the lumens of the wood. Figure 16.1 is a scanning electron microscopy (SEM) micrograph of unmodified wood showing open cells that are susceptible to indentation and wear. In contrast, Figure 16.2 is a micrograph of wood after impregnation and polymerization showing the voids filled with polymer that will resist indentation and wear.

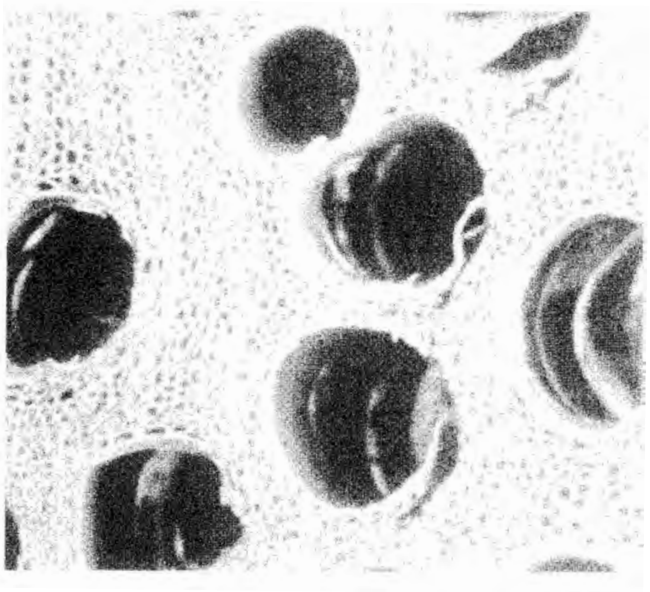


FIGURE 16.1 SEM micrograph of solid wood before polymer impregnation with open lumens.

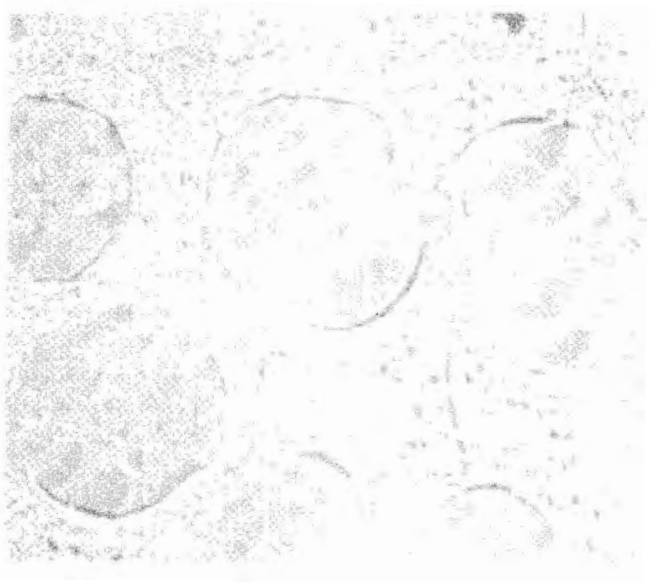


FIGURE 16.2 SEM micrograph of solid wood after polymer impregnation with filled lumens.

The process for impregnating wood with acrylics involves drying the wood (usually at 105°C) overnight to remove moisture, and then weighing. The wood is placed in a container (large enough for the wood, and an equal volume of solution), and a weight is placed on top of the wood to hold it under the solution. A vacuum (0.7–1.3 kPa) is applied to the wood for 30 min. (It can be longer depending on the size of the wood to be treated.) The acrylic monomer solution (containing the acrylic monomer, a catalyst [such as azo compounds] and perhaps a cross linking agent) is introduced into the container. The vacuum is maintained for 5–10 min to remove air from the monomer. The vacuum is then released, and the chamber returned to atmospheric conditions. The wood and solution are allowed to stand for usually 30 min. If the wood specimens have large dimensions, or are hard to penetrate species, then pressure is applied. The amount of pressure and time under pressure depends again on the size of the wood to be treated. Pressure is applied for 30 min, released, and again the wood is allowed to soak in the solution for 30 min. The treated wood is removed from the solution, drained, and wiped to remove excess chemical from the outside of the specimens. The monomer in the wood can be cured by either heat or irradiation. With heat, the chamber itself can be heated, or the wood can be removed from the chamber and heat cured in an oven or heated press. If polymerizing by heat, then the temperature is described by the catalyst, that is, Vazo 67 is heated at around 67°C. Those monomers that do not polymerize in the presence of air require a curing environment without air present. Heat is applied usually overnight or until the monomer has polymerized in the wood. Samples are weighed again, and percentage weight gain calculated. Some polymer will be on the surface of the wood and is sanded off.

There are many sources of acrylics and many different types of acrylics. Some monomers will be discussed in this chapter. The general one is methyl methacrylate. The thickness of the piece of wood being treated will determine the amount of pressure and/or vacuum needed. Small thin pieces of wood may not need any vacuum.

16.2 POLYMERIZATION METHODS

Free radicals used to initiate polymerization can be generated in two ways—by temperature sensitive catalysts or radiation curing. Chemical curing is a cheaper method with small-scale productions, while gamma radiation is more economical on a larger scale (Lee 1969).

A free radical catalyst or gamma-irradiated monomer generates the free radicals ($R\bullet + R\bullet$).

Initiation Step: $R\bullet + M$ (monomer) $+$ $R\text{-}M\bullet$
Propagation Step: $R\text{-}(M)_n\text{-}M\bullet + M - R\text{-}(M)^{n-1}\text{-}M\bullet$
Termination Step: $R\text{-}(M)_n\text{-}M\bullet + R\text{-}(M)_n\text{-}M\bullet - R\text{-}(M)_n\text{-}M\text{-}M\text{-}(M)_n\text{-}R$

16.2.1 CHEMICAL INITIATORS

16.2.1.1 Peroxides

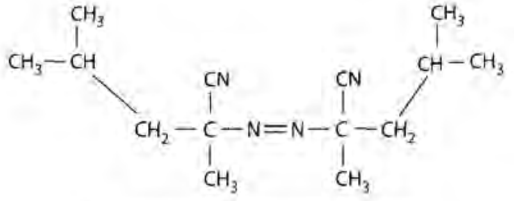
Peroxides form free radicals when thermally decomposed. These radicals initiate polymerization of vinyl monomers. Some peroxides used to initiate polymerization of monomers in wood include t-butyl hydroperoxide, methyl ethyl ketone peroxide, lauroyl peroxide, isopropyl hydroperoxide, cyclohexanone peroxide, hydrogen peroxide, and benzoyl peroxide. Each of the radicals generated from these peroxides has a different reactivity. The phenyl radical is more reactive than the benzyl radical, and the allyl radical is unreactive. Benzoyl peroxide is the most commonly used initiator. Usually the amount of peroxide added ranges from 0.2% to 3% by weight of monomer.

16.2.1.2 Vazo Catalysts

Dupont manufactures a series of catalysts with the trade name Vazo® that are substituted azonitrile compounds. The catalysts are white crystalline solids that are soluble in most vinyl monomers.

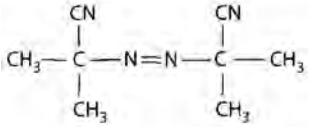
Upon thermal decomposition, the catalysts decompose to generate two free radicals per molecule. Nitrogen gas is also generated. The grade number is the Celsius temperature at which the half-life in solution is 10 h. The series consists of

Vazo® 52, the low-temperature polymerization initiator,



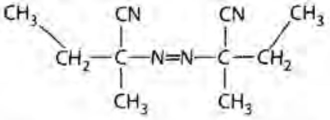
2,2′-azobis-2,4-dimethylvaleronitrile

Vazo® 64, also known as AIBN, (toxic tetramethylsuccinonitrile (TMSN) is produced, therefore better to substitute Vazo 67),



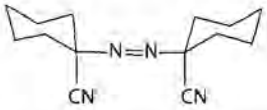
2,2′-azobisisobutyronitrile

Vazo® 67, best solubility in organic solvents and monomers,



2,2′-azobis-(2-methylbutyronitrile)

and Vazo® 88,



1,1′-azobis-(cyclohexanecarbonitrile)

Vazo® free radical initiators are solvent soluble and have a number of advantages over organic peroxides. They are more stable than most peroxides, so they can be stored under milder conditions. and are not shock-sensitive. They decompose with first-order kinetics, are not sensitive to metals. acids, and bases, and they are not susceptible to radical-induced decompositions. The Vazo catalysts produce less energetic radicals than peroxides, so there is less branching and cross-linking. The) are a weak oxidizing agent, which lets them be used to polymerize unsaturated amines, mercaptans. and aldehydes without affecting pigments and dyes.

Catalysts are most frequently used in concentrations of 1% or less by weight of the monomers. The rate of free radical formation is dependent on the catalyst used and is controlled by regulating the temperature. For Vazo 52, the temperature range is 35°C to 80°C; for Vazo 64 and Vas0 67,45°C to 90°C; and for Vazo 88,80°C to 120°C.

AIBN and cyclohexanone peroxide were used to initiate the polymerization of styrene in birchwood (Okonov and Grinberg 1983). Benzoyl peroxide or AIBN were used as initiators for beech wood impregnated with trimethylolpropane trimethacrylate and polyethylene glycol dimethacrylate (Nobashi et al. 1986). Buna sapwood was impregnated with tetraethylene glycol dimethacrylate containing AIBN as initiator (Nobashi et al. 1986). WPC were prepared from wood by impregnating with a mixture of unsaturated polyester, MMA, styrene and AIBN or benzoyl peroxide followed by heat-curing (Pesek 1984). Wood materials such as birch wood, basswood, and oak wood were impregnated with MMA or unsaturated polyester-styrene containing AIBN or benzoyl peroxide and polymerized. The polymerization was faster in the presence of AIBN than with benzoyl peroxide (Kawakami and Taneda 1973). Free radical copolymerization of glycidyl methacrylate (GMA) and *N*-vinyl-2-pyrrolidone was carried out using AIBN, in chloroform at 60°C (Soundararaian and Reddy 1991).

16.2.1.3 Radiation

There are two main radiation-initiated polymerization methods used to cure monomers in wood: gamma radiation and electron beam.

16.2.1.3.1 Gamma Radiation

Wood is a mixture of high molecular weight polymers; therefore, exposure to high-energy radiation will depolymerize the polymers, creating free radicals to initiate polymerization. With gamma radiation, polymerization rate and extent of polymerization are dependent on the type of monomer, other chemical additives, wood species, and radiation dose rate (Aagaard 1967). An example of radiation polymerization of the vinyl monomer MMA using cobalt 60 gamma ray dose rates of 56, 30, and 9 rad/s produced exotherms at 120°C, 90°C, and 70°C, respectively, with reaction times of 5, 7, and 12 h, respectively, produced 70–80% wood weight gain (Glukhov and Shiryaeva 1973). A 1.5–2.5 megarad-dose of gamma irradiation from a cobalt 60 source of isotope activity 20,000 Ci can be used to polymerize MMA in wood. Addition of a solid organic halogen compound with a high content of Cl or Br, accelerates the polymerization (Pesek et al. 1969). Addition of tributyl phosphate accelerates the polymerization rate of MMA 2.5 times and decreases the required radiation dosage. Addition of alkenyl phosphonates or alkenyl esters of phosphorus acids increases the polymerization rate and imparts fire resistance and bioresistance to the resultant WPC (Schneider, Phillips et al. 1990). Pietrzyk reports the optimum irradiation conditions for MMA in wood are: irradiation dose 1.5 Mrad and dose strength approximately 0.06 Mrad/h (Pietrzyk 1983). It is best if the irradiation is done in a closed container without turning the samples in order to minimize the escape of the monomer from the wood. Beech wood impregnated with MMA alone or in carbon tetrachloride or methanol solutions, can be cured with cobalt 60 gamma-radiation giving polymer loadings of up to 70% by weight. Radiation doses of 2–4 Mrad are necessary for complete conversion (Proksch 1969).

Moisture in wood accelerates polymerization (Pesek et al. 1969). A small amount of water in the wood or monomer improves the properties of the WPC (Pietrzyk 1983). The polymerization rate of MMA in beech wood is increased by using aqueous emulsions containing 30% MMA and 0.2% oxyethylated fatty alcohol mixture instead of 100% MMA. The complete conversion of MMA required ~5 kJ/kg radiation dose when the aqueous emulsions were used, in comparison to >16 kJ/kg when 100% MMA was used. The radiation polymerization of MMA in wood is inhibited by lignin (Pullmann et al. 1978).

Polymerization rate of vinyl compounds in wood, by gamma-ray irradiation, decreases in the presence of oxygen giving SO–90% conversion for styrene, methyl-, ethyl-, propyl-, and butyl methacrylates, and 4–8% conversion of vinyl acetate. Toluene diisocyanate addition increases monomer conversion, and decreases benzene extractives from the composite (Kawase and Hayakawa 1974).

The U.S. Atomic Energy Commission sponsored research that used gamma radiation to make WPC's in the early 1960s, but one drawback is the safety concerns and regulations needed when using radiation. Some advantages are that the monomer can be stored at ambient conditions, as long as inhibitor is included, and the rate of free radical generation is constant for cobalt-60 and does not increase with temperature (Meyer 1984).

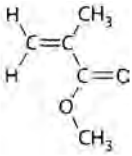
16.2.1.3.2 Electron Beam

High-energy electrons are another way of generating free radicals to initiate polymerization, and have been used with some success. Electron beam irradiation was used to make WPC's of beech sapwood veneers with styrene, MMA, acrylonitrile, butyl acrylate, acrylic acid, and unsaturated polyesters (Handa et al. 1973; Handa et al. 1983). Gotoda used electron beam to polymerize several different monomers and monomer combinations in wood (Gotoda et al. 1970a,b; Gotoda and Takeshita 1971; Gotoda et al. 1971, 1974, 1975; Gotoda and Kitada 1975). Increasing the wood moisture content has a positive effect on electron curing. For example, the monomer conversion in the electron beam-induced polymerization of MMA pre-impregnated in beech veneer increases with increases of moisture content in the wood up to 20–30% moisture, and is proportional to the square root of the electron dosage. The polymerization of styrene and acrylonitrile in veneer is also affected similarly by moisture content (Handa et al. 1973).

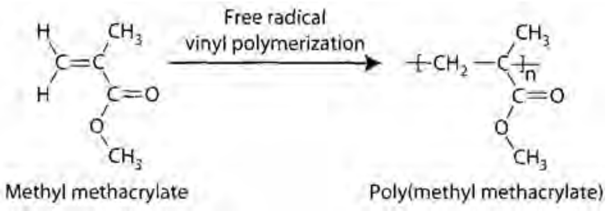
Some studies have indicated that curing of monomer systems in wood causes some interaction of the polymer with the wood. WPCs made with MMA, MMA-5% dioxane, and vinyl acetate impregnation into the wood cellular structure. followed by electron-beam irradiation show an increase in the compressive and bending strength, indicating some interaction at the wood–polymer interface (Boey et al. 1985). The dynamic modulus of WPC made from beech veneer impregnated with acrylic acid and acrylonitrile containing unsaturated polyester or polyethylene glycol methacrylate by electron beam irradiation, increased logarithmically as the weight polymer fraction increased, suggesting an interaction between the polymer and cell wall surface. The temperature dispersion of the dynamic viscoelasticity of composites also indicate an interaction between polymer and wood cell walls (Handa et al. 1981).

16.3 MONOMERS

16.3.1 ACRYLIC MONOMERS



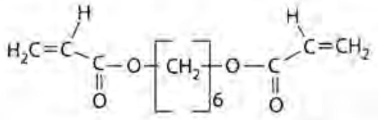
Methyl methacrylate (MMA) is the most commonly used monomer for WPCs (Meyer 1965). It is one of the least expensive and readily available monomers and is used alone or in combination with other monomers to cross-link the polymer system. MMA has a low boiling point (101°C) that can result in significant loss of monomer during curing and it must be cured in an inert atmosphere, or at least in the absence of oxygen. MMA shrinks about 21% by volume after polymerization, which results in some void space at the interface between the cell wall of the wood and the polymer. Adding cross-linking monomers such as di- and tri-methacrylates increases the shrinkage of the polymer which results in larger void spaces between the polymer and cell walls (Kawakami et al. 1981). Polymerization of MMA is exothermic and a lot of heat is generated during the polymerization that must be controlled.



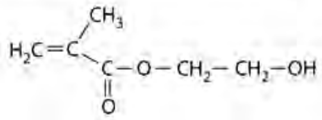
MMA can be polymerized in wood using catalysts (Vazo or peroxides) and heat, or radiation. Curing of MMA using cobalt-60 gamma radiation requires a longer period of time (8–10 h depending upon the radiation flux) while catalyst-heat-initiated reactions are much faster (30 min or less at 60°C) (Meyer 1981).

Hardness modulus values determined for untreated and poly methyl methacrylate-treated red oak, aspen, and sugar maple, on both flat and edge-grained faces show untreated wood hardness values are related to sample density. There are significant relationships between treated wood hardness modulus, wood density, and loading. Large variations in hardness modulus of treated aspen and maple are related to their diffuse-porous structure. In contrast, the hardness modulus of treated red oak is predictable on the basis of density or polymer loading (Beall et al. 1973).

The compressive and bending strengths of a tropical wood *(Kapur-Dryobalanops* sp.) are improved significantly by impregnation of MMA (Boey et al. 1985). Using a gamma irradiation method, some tropical wood-poly methyl methacrylate and–poly(vinyl acetate) composites are produced which exhibit a significant improvement in uniaxial compressive strength (Boey et al. 1987). Samples with an average polymer content of 63% (based on dry wood) show increases in compressive strength, toughness, radial hardness, compressive strength parallel to the grain, and tangential sphere strength (Bull et al. 1985). Hardness and mechanical properties of poplar wood are improved by impregnation with MMA and polymerization of the monomer by exposure to gamma-irradiation, the hardness of the product increases with impregnation pressure and weight of polymer (Bull et al. 1985; Ellis 1994).



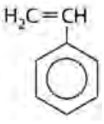
1,6-Hexanediol diacrylate (HDDA)



2-Hydroxyethyl methacrylate (HEMA)

Various other acrylic monomers have been investigated (Ellis and O’Dell 1999). WPCs were made with different chemical combinations and evaluated for dimensional stability, ability to exclude water vapor and liquid water, and hardness. Different combinations of hexanediol diacrylate (HDDA), hydroxyethyl methacrylate (HEMA), hexamethylene diisocyanate (Desmodur N75, DesN75), and maleic anhydride (MAn) were *in situ* polymerized in solid pine, maple and oak wood. The rate of water vapor and liquid water absorption was slowed, and the rate of swelling was less than that of unmodified wood specimens, but the dimensional stability was not permanent (see Figure 16.3). The WPCs were much harder than unmodified wood (see Table 16.1). Wetting and penetration of water into the wood was greatly decreased, and hardness and dimensional stability increased with the chemical combination of hexanediol diacrylate, hydroxyethyl methacrylate, and hexamethylene diisocyanate. Treatments containing hydroxyethyl methacrylate were harder and excluded water and moisture more effectively. This is probably due to the increased interfacial adhesion between the polymer and wood, due to the polarity of HEMA monomer.

16.3.2 STYRENE



Styrene is another monomer that is commonly used for WPCs. It can be polymerized in wood using catalysts (Vazo or peroxides) and heat, or radiation. Other monomers are commonly added to

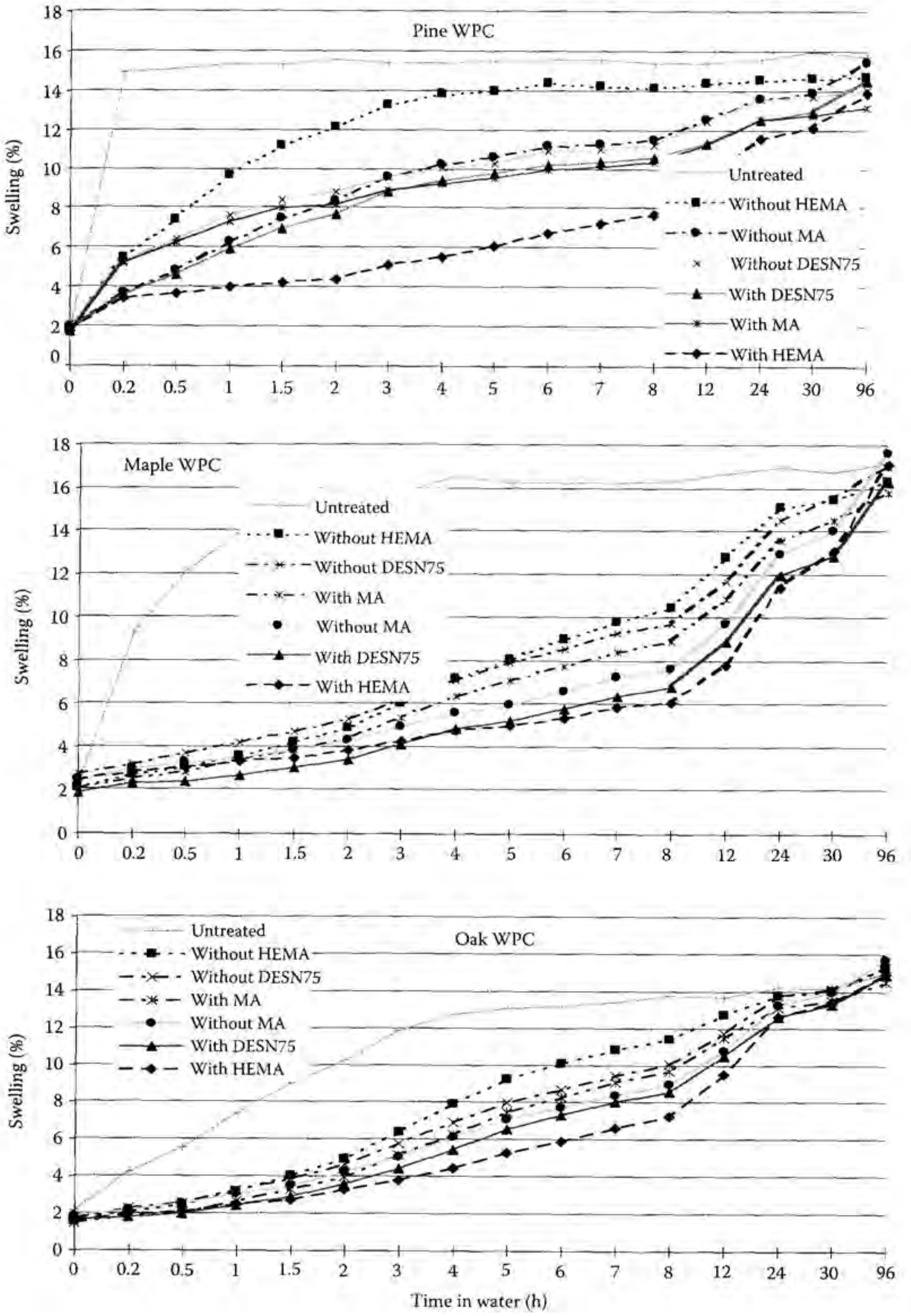


FIGURE 16.3 Volumetric swelling of WPC specimens in water.

TABLE 16.1
The Rockwell Hardness of WPC Specimens

Treatment	Earlywood	Latewood
Pine		
HDDA/DesN75 (3:1)	37.3	45.0
HDDA	32.2	41.9
HDDA/MA (3:1)	31.7	26.0
HDDA/HEMA/MA (1:2:1)	61.7	67.8
HEMA/DesN75/MA (2:1:1)	61.0	70.1
HDDNDesN75MA (2:1:1)	31.7	49.3
HDDA/HEMA (1:1)	47.0	55.3
HDDA/HEMA/DesN75 (1:2:1)	63.2	74.2
CONTROL (untreated)	−15.5	−10.6
Maple		
HDDA/DesN75 (3:1)	44.8	
HDDA	46.8	
HDDAlMA (3:1)	49.2	
HDDA/HEMA/MA (1:2:1)	60.0	
HEMA/DesN75/MA (2:1:1)	56.4	
HDDNDesN75MA (2:1:1)	46.6	
HDDA/HEMA (1:1)	49.5	
HDDA/HEMA/DesN75 (1:2:1)	65.6	
CONTROL (untreated)	−9.4	
Red Oak		
HDDNDesN75 (3:1)	23.3	22.7
HDDA	27.9	25.1
HDDA/MA (3:1)	23.1	20.5
HDDA/HEMA/MA (1:2:1)	38.6	46.3
HEMA/DesN75/MA (2:1:1)	26.8	35.4
HDDA/DesN75/MA (2:1:1)	23.0	13.6
HDDA/HEMA (1:1)	29.6	25.5
HDDA/HEMA/DesN75 (1:2:1)	39.3	40.8
CONTROL (untreated)	−17.1	−25.1

Note: Rockwell hardness of the longitudinal face of 25 × 25 × 0.6 mm^3 specimens. 1/4 inch ball indenter and 60 Kgf (Rockwell scale L). Maple measured without regard to earlywood or latewood.

control the polymerization rate, extent of polymerization, and to cross-link the styrene for improved physical properties of the WPCs.

Hardness, impact strength, compression and shear strength, and bending and cleavage strengths of styrene treated wood are better than for untreated samples and the same as, or better than, those for samples impregnated with MMA. The treated wood is sometimes unevenly colored and more yellow than the original samples (Autio and Miettinen 1970).

Modification of several types of hard- and softwoods with polystyrene improves their resistance to wear. Wood–polystyrene composites made from the softwood species birch, gray and black alder, and spruce exhibits abrasion resistance comparable to that of natural oakwood (Dolacis 1983). The flexural strength, hardness, and density of alderwood are increased by impregnating it with styrene and heating to obtain the polystyrene saturated wood (Lawniczak 1979). Poplar wood modified with polystyrene has increased hardness, static bending strength and toughness; the increases in toughness depend on the polymer content to a certain limit (Lawniczak 1973).

WPC can be prepared from a mixture of acrylonitrile–styrene–unsaturated polyester in wood. This mixture gives a tough cross-linked polymer, and is more favorable for radiation polymerization than the systems of MMA, MMA unsaturated polyester, and acrylonitrile-styrene (Czvikovszky 1977, 1981). Composite materials obtained by evacuation of wood (beech, spruce, ash, and tropical wood *Pterocarpus vermalis)* followed by its impregnation with an unsaturated polyester–MMA–styrene mixture or unsaturated polyester–acrylonitrile–styrene mixture and gamma-irradiation-induced curing exhibit decreased water vapor absorption and improved dimensional stability, hardness, compression strength, and wear resistance, compared to untreated wood (Czvikovszky 1982).

Curing of unsaturated polyester–styrene mixture can be affected by the initiator-heat technique by either using 0.1–0.2% benzoyl peroxide or 1% methyl ethyl ketone peroxide (Doss et al. 1991). Polymer-reinforced alderwood can be prepared by impregnating it with styrene and peroxide catalyst, followed by thermal polymerization for 3–7 h. The addition of 1.0% divinylbenzene, triallyl phosphate, or trimethylolpropane trimethacrylate cross-linking agent to styrene results in an increased polymerization rate, with divinylbenzene having the most pronounced effect on the polymerization rate (Lawniczak and Szwarc 1987). Gamma-ray-induced polymerization of styrene in impregnated samples of beech wood in the presence of carbon tetrachloride require a minimum dose of 159 kGy for full monomer hardening. The polymer content in the resulting samples is 53% at a monomer conversion of >90%. A modified sample has ~50% increase in density, ~90% increase in hardness, and ~125% decrease in absorptivity, compared to unmodified wood (Raj and Kokta 1991).

The impregnation of beech wood with ternary mixtures of styrene, dioxane, acetone, or ethanol. and water then curing by ionizing radiation gives a product with some dimensional stability due to chemical fixation of the polymer on the lignocellulosic material. This change is accompanied by a marked change in the structure of the cell wall. Pure styrene or styrene in aqueous solution gives a composite with low-dimensional stability (Guillemain et al. 1969). Wood polymers based on aqueous emulsion polyester–styrene mixtures are dimensionally more stable than those produced with a pure polyester–styrene mixture (Jokel 1972). Impregnation of poplar wood with styrene–ethanol–water followed by polymerization at 70°C gives 50% increase in dimensional stability with 30–40% polystyrene content in the wood. Use of styrene alone increased wood dimensional stability by only 10% even with >100% styrene retention. Dimensional stability of poplar wood is also significantly increased (~40%) by a 90:5 styrene–ethanol system (Katuscak et al. 1972). The use of a mixture of polar solvents with styrene to make WPC seems to improve the dimensional stability of the composites. The use of styrene alone for the modification of wood was not as favorable as using a styrene–methanol–watersystem which gives greater bending strength and better dimensional stability. Hardness increases with increasing polystyrene in the wood (Varga and Piatrik 1974).

Untreated woods of ash, birch, elm, and maple, absorb about 4 times more water than woods containing acrylonitrile–styrene copolymer (Spindler et al. 1973). Addition of acrylonitrile and butyl methacrylate to styrene does not affect significantly the maximum amount of water sorbed by the composites but decreases their swelling rate and increases their dimensional stability and bending strength (Lawniczak and Pawlak 1983). WPC prepared using styrene–acrylonitrile have increased hardness, substantially improved dimensional stability, and give no difficulties in machining and gluing (Singer et al. 1969).

Monomer- and polyester prepolymer-impregnated beech wood veneer irradiated with 3–6 Mrads and cured at 80°C has improved shrinkage resistance and water repellency and provides laminates suitable for flooring and siding. Various mixtures of unsaturated polyester and styrene, as well as the individual monomers MMA, ethyl acrylate, butyl acrylate, acrylonitrile, and vinyl acetate haw been used to treat veneers. A variety of tests of physical properties show the styrene–polyester system to be superior (Handa et al. 1972).

WPCs can be prepared by gamma irradiation of hardwood impregnated with a styrene-unsaturated polyester mixture, MMA, or acrylonitrile–styrene mixture. The addition of chlorinated paraffin oil to any of these monomer systems imparts fire resistance to the composites and reduces the gamma-ray dosage needed for total polymerization of the monomers. Styrene-unsaturated polyester mixtures containing about 30% chlorinated paraffin oil are suitable systems for large-scale preparation of composites (Iya and Majali 1978).

Modification of wood samples with polystyrene increases the resistance of the composites to degradation in contact with rusting steel (Helinska-Raczkowska and Molinski 1983). Conversion of unsaturated polyester–styrene mixture and dimensional stability of the wood–styrene–unsaturated polyester composites decreases with an increase in moisture content of the wood to be treated (Yamashina et al. 1978).

Polymerization of styrene in wood can result in the grafting of styrene to cellulose, lignin, and pentosans (Lawniczak et al. 1987). The treatment of wood with diluted hydrogen peroxide solution leads to an increase in the viscosity-average molecular weight of the polystyrene, and to the graft polymerization of the monomer, which, in turn, enhances the stress properties of wood–polystyrene composites (Manrich and Marcondes 1989).

Wood impregnated with a styrene–ethylene glycol dimethacrylate mixture under full vacuum (0.64 kPa), has higher densities and hardness in the early wood than that of late wood, and early wood shows hardness increases roughly double those in late wood at the same density, indicating styrene uptake is predominantly in early wood (Brebner et al. 1985).

Kenaga (1970) researched high boiling styrene-type monomers including vinyltoluene, tert-butylstyrene, and *o*-chlorostyrene. In the preparation of WPCs the cure rate, monomer loss, and composite physical properties can be varied by appropriate selection and concentration of catalyst, comonomers, and cross-linking agents. The composite can be bonded to untreated crossbanded veneers simultaneously with polymerization in a press because these three styrene-type monomers have boiling points from 27°C to 74°C higher than styrene's boiling point. The monomer tert-butylstyrene has the highest boiling point at 219°C and the least shrinkage, 7%, on polymerization. Cross-linking agents increase reaction rate and improve the WPC physical properties. Effects of the cross-linking agents trimethylolpropane triacrylate, trivinyl isocyanurate, trimethylolpropane trimethacrylate, ethylene glycol dimethacrylate, trimethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, and divinylbenzene were studied. Generally 10% or more cross-linking agent is needed to give the best improvement in abrasion resistance. Copolymers of tert-butylstyrene with di-ethyl maleate, di-ethyl fumarate, and acrylonitrile were studied in basswood and birch wood blocks. All the copolymers except acrylonitrile improved the abrasion resistance of the composite. Polyesters lowered cure time and styrene monomer loss during cure but increased the exotherm temperature to a level that could be unacceptable for larger pieces of wood.

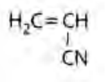
16.3.3 POLYESTERS

Unsaturated polyester resins are most often used in combination with other monomers, making them less expensive and improving their properties. Many polyester resins are available as commercial products. Polyester, MMA, and styrene were polymerized individually and in combinations by gamma radiation or benzoyl peroxide (Miettinen et al. 1968; Miettinen 1969). MMA composites had higher tensile strength and abrasion resistance, but lower bending strength and impact strength compared to the polyester composites. Styrene is frequently mixed with polyester resins to reduce viscosity, thus enabling better penetration into the wood. Polyesters decrease the loss of styrene monomer, and the time to heat cure (Kenaga 1970).

16.3.4 MELAMINE RESINS

Melamine resins have many uses with paper and wood products. Paper can be impregnated with melamine resins, and then laminated to the surface of wood veneers, fiber boards, or other panel products resulting in a hard, smooth, and water resistant surface. Wood veneers can also be impregnated with melamine resins to improve dimensional stability, water resistance, and hardness (Inoue et al. 1993; Takasu and Matsuda 1993). The melamine resin-modified wood is 1.5–4 times harder than untreated wood (Inoue et al. 1993). Yet, the maximum hardness achieved by melamine modified wood is less than that of wood modified with acrylate, methacrylate, and other vinyl monomers which increase hardness 7–10 times that of unmodified wood (Mizumachi 1975). But, the hardness of melamine resin-impregnated wood can be increased by compressing the wood (Inoue et al. 1993). The melamine resins decrease the abrasion resistance of wood (Inoue et al. 1993; Takasu and Matsuda 1993).

16.3.5 ACRYLONITRILE



$$H_2C{=}CH(CN)$$

Acrylonitrile is used in the production of WPCs mostly in combination with other monomers because the polymer does not improve properties by itself. It is most frequently used with styrene. and less frequently with MMA, methyl acrylate, unsaturated polyester, diallyl phthalate, and vinylidene chloride. WPCs made with MMA–acrylonitrile or styrene–acrylonitrile mixtures were cured using either gamma radiation or catalyst, and the resultant composites were found to be very similar (Yap et al. 1990, 1991).

Styrene–acrylonitrile WPCs show high-dimensional stability which is probably due to swelling of the wood by the acrylonitrile during treatment creating a bulking action (Loos 1968). Addition of acrylonitrile to styrene gives substantial improvement in hardness and compressibility of the wood (Rao et al. 1968). Ratios of acrylonitrile to styrene between 7:3 and 4:1 give the most substantial improvements in dimensional stability, compressibility, and hardness. The antiswell efficiencies of wood–styrene–acrylonitrile combinations are 60–70% (no swelling is 100%) (Ellwood et al. 1969). Moisture absorption increases with increase of acrylonitrile in WPCs made with various ratios of acrylonitrile and methyl acrylate (Gotoda et al. 1970b).

Copolymerization of bis(2-chloroethyl) vinylphosphonate with vinyl acetate or acrylonitrile in beechwood improves the dimensional stability of the WPCs (Ahmed et al. 1971). A ternary resin mixture of styrene, acrylonitrile, and unsaturated polyester that can be cured in the wood with a low dose of gamma radiation also has favorable properties (Czvikovszky 1977, 1981, 1982).

The addition of acrylonitrile to a diallyl phthalate prepolymer improves the glueability of the composite against a substrate, such as plywood or particle board. The weatherability of a wood composite laminate containing diallyl phthalate prepolymer and acrylonitrile is improved by incorporating polyethylene glycol dimethacrylate (Gotoda et al. 1971).

Acrylonitrile is highly toxic and is a carcinogen therefore attempts have been made to find chemicals that can be substituted for acrylonitrile in the treating solutions. These attempts have been only partially successful. *N*-vinyl carbazol can be used as a partial replacement of acrylonitrile. Several other compounds including acryloamide, *N*-hydroxy acryloamide and 1-vinyl-2-pyrrolidone were tried unsuccessfully (Schaudy and Proksch 1982).

16.4 CROSS-LINKING AGENTS

Some of the cross-linking agents frequently used with MMA, styrene, or other vinyl monomers are trimethylolpropane triacrylate, trivinyl isocyanurate, trimethylolpropane trimethacrylate, ethylene glycol dimethacrylate, trimethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate. polyethylene glycol dimethacrylate, and divinylbenzene. Cross-linking agents generally increase reaction rate and improve the WPC’s physical properties (Kenaga 1970).

Several cross-linking monomers, including 1,3-butylene dimethacrylate ethylene dimethacrylate and trimethylolpropane trimethacrylate and the polar monomers 2-hydroxyethyl methacrylate and glycidyl methacrylate, were added at 5–20% concentration to MMA, and their effects upon the polymerization and properties of the composites were examined (Kawakami et al. 1977). WPCs with only MMA show a void space at the interface between cell wall and polymer. With addition of cross-linking esters such as di- and tri-methacrylate, the shrinkage (and hence void spaces) of the polymer during polymerization increases. On the other hand, in the WPCs containing polar esters having hydroxyethyl and glycidyl groups, the voids due to the shrinkage of polymer was found to form inside the polymer itself, suggesting better adhesion of the polymer to the inner surface of cell wall (Kawakami et al. 1981).

Impregnation with ethyl a-hydroxymethylacrylate (EHMA) plus another multifunctional monomer 2 vinyl-4,4-dimethyl 2-oxazolin-5-one (vinyl azlactone) results in improved mechanical properties of wood samples. Improvements of 38–54% in impact strength and 27–44% in compression modulus are achieved depending on the relative amount of vinyl azlactone incorporated (Mathias et al. 1991).

16.4.1 ISOCYANATES

The addition of isocyanate compounds with acrylic monomers reduces the brittleness of WPCs consisting only of acrylic compounds (Schaudy and Proksch 1981). WPC properties improve by adding a blocked isocyanate to a mixture of MMA and 2-hydroxyethyl methacrylate (Fujimura et al. 1990). The isocyanate compound cross-links the copolymer.

The mechanical properties of a wood–polystyrene composite are improved by the addition of an isocyanate compound to the styrene treating mixture. Polymethylene (polyphenyl isocyanate) forms a bridge between wood and polymer on the interfaces. The isocyanate compound then becomes instrumental in efficient stress transfer between the wood and polymer (Maldas et al. 1989).

16.4.2 ANHYDRIDES

A maleic anhydride and styrene mixture has been used to make WPCs (Ge, Peng et al. 1983). Also, a mixture of tetraethylene glycol dimethacrylate and chlorendic anhydride have been used to increase fire, chemical and abrasion resistance as well as hardness (Paszner et al. 1975). A process has been developed that is designed to prepare cross-linked oligoesterified wood with improved dimensional stability and surface properties. Maleic, phthalic, and succinic anhydrides are used. The wood is reacted with the anhydride then impregnated with glycidyl methacrylate then heated to cause cross-linking. In a one-step process the anhydride and glycidyl methacrylate are impregnated into the wood together, then polymerized and reacted with the wood simultaneously. The resulting wood is hard and has smooth surfaces. As the anhydride in the anhydride:glycidyl methacrylate ratio increases the dimensional stability increases (Ueda et al. 1992).

16.5 PROPERTIES OF WOOD–POLYMER COMPOSITES

WPCs can improve many properties of solid wood, and therefore be tailored for a specific application. Some of these properties are surface hardness, toughness, abrasion resistance, dimensional stability, moisture exclusion, and fire, decay and weather resistance. Table 16.2 is a summary of some of the properties of woods modified by five different treatments.

16.5.1 HARDNESS

Hardness is the property that resists crushing of wood and the formation of permanent dents. Hardness is, for the most part, a function of density, that is, the more dense the wood, the harder it is. The density of dry wood varies widely based on the volume of void (lumens and vessels) space in the wood. For example, the density of dry balsa wood ranges from 100 to 200 kg/m^3 with a typical density of about 140–170 kg/m^3 (about one-third the density of other hard woods) while a wood like lignum vitae has a density of 1280–1370 kg/m^3 (this wood does not float).

TABLE 16.2
Properties of Wood after Five Different Modifications

	Water-Soluble Polymers and Synthetic Resins		Compression		Heat	Organic Chemicals or Cross-Linking Agents		Liquid Monomers	
Property	**Polyethylene Glycol**	**Impreg**	**Staypak**	**Compreg**	**Staybwood**	**Bulking**	**Cross-Linking**	**Methyl Methacrylate**	**Epoxy Resin**
Specific gravity	Slightly increased	15–20 pct greater than normal wood	1.2–1.4	1.0–1.4	Unchanged	Slightly increased	Unchanged	Increased	Increased
Permeability to water vapor	Hygroscopic	Better than normal	Better than normal	Greatly improved	Better than normal	Unchanged	Unchanged	Greatly improved	Greatly improved
Liquid water repellency	Hygroscopic	Better than normal	Better than normal	Greatly improved	Better than normal	Better than normal	Better than normal	Greatly improved	Greatly improved
Dimensional stability	80 pct	60–70 pct	Slightly improved	80–85 pct	40 pct	65–75 pct	80–90 pct	10 pct	Slightly improved
Decay resistance	Better than normal	Better than normal	Unchanged	Much better than normal	Better than normal	Much better than normal	Better than normal	Somewhat increased	Somewhat increased
Heat resistance	No data	Greatly increased	No data	Greatly increased	No data	No data	No data	Increased	No data
Fire resistance	No data	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged	Unchanged	No data
Chemical resistance	No data	Better than normal	Slightly better than normal	Much better than normal	Better than normal	No data	No data	Much better than normal	Much better than normal
Compression strength	Slightly increased	Increased	Increased	Greatly increased	Reduced	Slightly reduced	Slightly reduced	Greatly increased	Greatly increased
Hardness	Unchanged	Increased	Increased	10–20 times greater	Reduced	Slightly reduced	Slightly reduced	Greatly increased	Greatly increased
Abrasion resistance	Slightly reduced	Reduced	Increased	Increased	Greatly reduced	Slightly reduced	Greatly reduced	Greatly increased	Greatly increased
Machinability	Unchanged	Better than normal but dulls tools	Metalworking tools required	Metalworking tools required	Unchanged	Unchanged	Unchanged	Metalworking tools preferred	Metalworking tools preferred
Glueability	Special glues required	Unchanged	Unchanged	Same as normal after sanding	Unchanged	Unchanged	Unchanged	Special glues required	Epoxy used as adhesive
Finishability	Requires poly, urethane, oil, or 2 parts polymer	Unchanged	Unchanged	Plastic-like surface (can be polished without finish)	Unchanged	Unchanged	Unchanged	Plastic-like Surface (no finish required)	Plastic-like surface (no finish required)
Color change	Little change	Reddish brown	Little change	Reddish brown	Darkened	Little change	Little change	Little change	Little change

The Janka Scale of Hardness measures the force required to embed a 1.11 cm (0.444 in.) steel ball to half its diameter in wood. It is the industry standard for determining the ability of various species to resist denting and wear. The Janka hardness of lignum vitae ranks highest of the trade woods, with a Janka hardness of 4500. Table 16.3 shows the Janka hardness of several domestic and foreign woods.

The hardness or indent resistance of WPC is measured by any of several methods. The test method used depends on the WPC and the expected final product. Measurement can be made using a hand-held Shore Durometer tester, ball indenters such as Brinell and Rockwell hardness, the Janka ball indenter or the Gardner Impact tester that uses a falling dart to make dents that can be measured (Miettinen et al. 1968; Beall et al. 1973; Schneider 1994).

Hardness of a WPC depends on the polymer loading and the hardness of the polymer. Polymer loading is affected by wood porosity and density. For example, a more porous and lower density wood will require a higher polymer loading. Generally, a higher polymer loading will give a greater WPC hardness. Figure 16.4 is an SEM micrograph of a WPC with no polymer attachment and the lumens incompletely filled. Figure 16.5 is an SEM micrograph of a WPC with filled lumens and some interaction of the polymer with the wood. The hardness of a WPC is improved when the cells are completely filled and there is attachment of the polymer to the wood.

TABLE 16.3
Janka Hardness of Hardwoods and Softwoods

Wood Species	Janka Hardness
Eastern white pine	380
Basswood	410
Chestnut	540
Douglas fir	660
Southern yellow pine	690
Sycamore	770
Cedar	900
Black cherry	950
Teak	1000
Black walnut	1010
Yellow birch	1260
Red oak	1290
American beech	1300
Ash	1320
White oak	1360
Hard maple	1450
Birch	1470
Brazilian oak	1650
Locust	1700
Rosewood	1780
Hickory	1820
Purple heart	1860
African rosewood	1980
Mesquite	2345
Brazilian cherry	2350
Brazilian rosewood	3000
Ebony	3220
Brazilian teak	3540
Brazilian walnut	3680

FIGURE 16.4 SEM micrograph of a WPC having the wood cells incompletely filled with polymer and having no attachment of polymer to the wood.

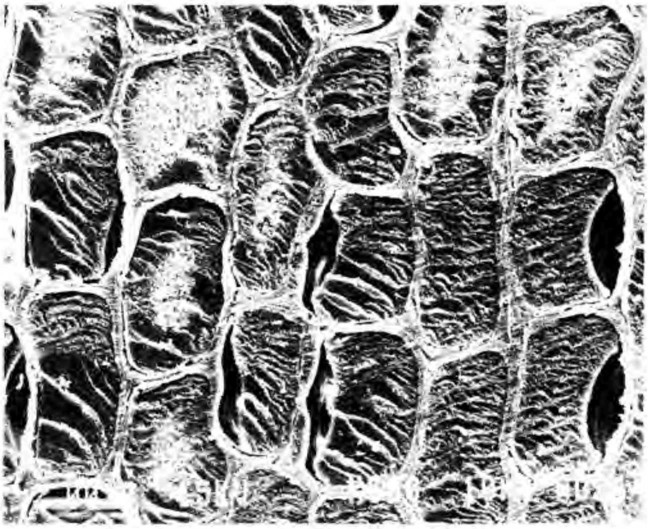


FIGURE 16.5 SEM micrograph of a WPC with the wood cells filled with polymer and having some interaction of the polymer with the wood.

The type of polymer, cross-linking chemicals and method and extent of polymerization affect polymer hardness. A 7–10-fold increase in hardness can be expected by most treatments for example, MMA-impregnated alderwood has more than a 10-fold increase in hardness of the sides and more than a 7-fold increase in hardness of the cross-cut areas (Miettinen et al. 1968).

16.5.2 TOUGHNESS

Increasing the toughness of wood with polymer increases the crack resistance and brittleness at room temperature. Impact strength and toughness are closely related; both refer to the WPCs ability to resist fracturing. Measurements of impact strength are made using the Izod and the Charpy impact test instruments. The test involves striking the specimen with a pendulum and measuring the impact energy necessary to initiate fracture. Treating sugar maple wood with a vinyl polymer increases toughness in both radial and tangential impact directions compared to untreated wood. Increased polymer load results in increased toughness. Microscopy indicates brittle polymer fracture extends across lumens but stops at the polymer and cell wall interface (Schneider et al. 1989). Brittleness of a composite can be severely increased by increasing the amount of a cross-linker such as ethyleneglycol dimethacrylate even to as little as 1.5% in MMA (Schaudy and Proksch 1982). WPC’s with high toughness (low brittleness), have been prepared by using a treating mixture consisting of MMA and an isocyanate that has an acrylic functionality. This treating mixture increased the impact bending strength of the WPC by about 100% (Schaudy et al. 1982).

16.5.3 ABRASION RESISTANCE

Abrasion resistance is determined by the Taber wear index, which is the weight loss (mg/1000 cycles) caused by an abrasive wheel turning on a specimen. The lower the weight loss value, the better the resistance to wear. In general, abrasion resistance increases with increasing polymer content in the wood (Kawakami and Taneda 1973). Softwood species such as birch, gray and black alder, and spruce when made into a composite with polystyrene have abrasion resistance comparable to that of natural oak wood (Dolacis 1983). Alder wood and birch wood impregnated with MMA had up to 85% less weight loss than untreated wood (Miettinen et al. 1968).

16.5.4 DIMENSIONAL STABILITY

Dimensional stability is the property of wood that allows it to resist changes in dimensions when exposed to various moisture conditions. Dimensional stability is reported as percent volumetric swelling or as antishrink efficiency (ASE). ASE is the percent reduction in volumetric swelling of treated wood compared to untreated wood at equilibrium water or moisture saturated conditions (see Chapter 4). Many WPCs are not dimensionally stable so that with time in water or high humidity, most WPCs will swell to the same amount as untreated wood.

There are two approaches to improve the dimensional stability of WPCs. One approach is to direct the penetration into the wood cell walls to bulk the wood at or near its wet or green dimensions. Aqueous and nonaqueous solvents have been used to swell the wood and carry the monomers into the cell walls, and polar monomers have been used to increase the swelling of the wood and penetration of the monomers into the wood. The second approach is to react the chemicals with the cell wall hydroxyl groups, therefore decreasing its affinity for moisture (Loos 1968; Rowell1 et al. 1982). WPCs with polymer located just within the lumen do not make a significant contribution to dimensional stability compared with chemical modifications of the cell wall (Fujimura and Inoue 1991).

16.5.5 MOISTURE EXCLUSION

Moisture exclusion efficiency (MEE) is the property of a WPC to exclude moisture and is related to the rate at which the composite absorbs moisture and swells and not to the maximum extent of swelling or moisture uptake (see Chapter 4). If the WPCs are not allowed to reach equilibrium with respect to moisture or water, then MEE can be mistaken for dimensional stability or ASE values (Loos 1968). Many WPCs will absorb water and swell at a slower rate than untreated wood, but in most cases the maximum swelling is nearly the same as that of untreated wood.

16.5.6 FIRE RESISTANCE

There are several methods of measuring different aspects of the property of fire retardancy (see Chapter 6). Thermogravimetry measures char formation and decomposition temperatures by heating small specimens in an inert atmosphere. More char generally indicates greater fire retardancy. The oxygen index test measures the minimum concentration of oxygen, in an oxygen and nitrogen atmosphere, that will just support flaming combustion. Highly flammable materials are likely to have a low oxygen index. Flame spread tests are those in which the duration of flaming and extent of flame spread are measured. The results of any of the test methods that use small specimens often do not correlate with the actual performance of materials in a real fire situation. The surface burning characteristics of WPCs used as building materials are best measured by flame spread tests that use large specimens, such as the ASTM E84 test that requires specimens approximately 514 mm wide by 7.3 m long. The test chamber in this test also has a photometer system built in to measure smoke and particulate density. Smoke evolution is very important because many fire deaths are due to smoke inhalation.

Polymethyl methacrylate enhances the flammability of wood (Calleton et al. 1970; Lubke and Jokel 1983) but not styrene and acrylonitrile (Schaudy et al. 1982). Bis(2-chloroethyl) vinylphosphonate with vinyl acetate or acrylonitrile improves the fire retardancy, but is less effective than poly(dichlorovinyl phosphate) or poly(di-ethyl vinylphosphonate). Wood impregnated with dimethylaminoethyl methacrylate phosphate salt and then polymerized in the presence of cross-linking agents has high fire retardancy (Ahmed et al. 1971) as does trichloroethyl phosphate (Autio and Miettinen 1970). The addition of chlorinated paraffin oil to monomer systems imparts fire retardancy to composites (Iya and Majali 1978). The limiting oxygen index values of the MMA-bis(2-chloroethy1)vinyl phosphonate copolymer and MMA-bis(chloropropyl)-2-propene phosphonate copolymer wood composites are much higher than that of untreated wood and other composites, indicating the effectiveness of the phosphonates as fire retardants (Yap et al. 1991). WPC specimens made with MMA are smoke free, but styrene-type monomers create dense smoke (Siau et al. 1972). The presence of aromatic polymers, such as poly(chlorostyrene), and fire retardants having aromatic benzene rings in wood increase the smoke evolution, flame spread, and fuel contribution in a modified tunnel furnace test (Siau et al. 197.5). In all specimens tested, the smoke evolution increased markedly after the flame is extinguished.

16.5.7 DECAY RESISTANCE

Most WPCs are not decay resistant because the polymer merely fills the lumens and does not enter the cell walls, which makes the cell walls accessible to moisture and decay organisms (see Chapter 5). WPCs prepared using MMA and several kinds of cross-linking monomers (1,3-butylene dimethacrylate, ethylene dimethacrylate, and trimethylolpropane trimethacrylate) and polar monomers (2-hydroxyethyl methacrylate and glycidyl methacrylate) added at 5–20% concentration have little resistance to brown rot decay (Kawakami et al. 1977). Using methanol with MMA or styrene allows the polymer to penetrate the cell walls. The amount of polymer in the cell wall is important for decay resistance. Some protection against biological degradation is possible at cell wall polymer contents of 10% or more (Rowell 1983). Acrylate monomers with various bioactive moieties were synthesized (Ibach and Rowell 2001). Pentachlorophenol acrylate and Fyrol 6 acrylate polymers provided no protection against decay, whereas tributyltin acrylate, 8-hydroxyquinolyl acrylate, and 5,7-dibromo-8-hydroxyquinolyl acrylate were found to be resistant to the brown-rot fungus *Gloeophyllum trabeum* at low polymer loading of 2–5% retention (Ibach and Rowell 2001).

16.5.8 WEATHERING RESISTANCE

WPCs made with birch and pine, impregnated with MMA or styrene–acrylonitrile were exposed in a weatherometer for 1000 h (Desai and Juneja 1972). The specimens were more resistant to surface checking than untreated wood and the styrene–acrylonitrile treatment performed better than MMA.

A combination of cell wall-modifying treatments (butylene oxide or methyl isocyanate) with MMA lumen-filled treatments results in a dual treatment that resists the degradative effects of accelerated weathering in a weatherometer (see Chapter 7). The use of MMA in addition to the cell wall-modifying chemical treatments provides added dimensional stability and lignin stabilization and has a significant effect on weatherability (Rowel1 et al. 1981).

16.5.9 MECHANICAL PROPERTIES

The strength properties of WPCs are enhanced compared to untreated wood. The hardness, compression and impact strength of wood composites increase with increasing monomer loading (Mohan and Iyer 1991). Cross-linking monomers increases static bending properties, compressive strength, and torsional modulus, but reduces dimensional stability, while polar monomers improve dimensional stability and static bending properties but have no significant effect on compressive strength and torsional modulus (Kawakami et al. 1977). Table 16.4 shows the increase in strength properties of acrylic lumen filled wood. All strength properties are greatly improved.

16.5.10 CHANGES IN COLOR

Dyes can be added to the monomer solution to change the color of the polymerized wood. Figure 16.6 shows natural oak on the left and a dark dyed oak on the right. Figure 16.7 shows a knife handle made from several layers of natural and dyed veneers.

TABLE 16.4
Strength Properties of Acrylic Lumen Filled Wood

Static Bending Properties of Acrylic Lumen Filled Wood

Property	Untreated MPa	Treated MPa
MOE	9.3	11.6
FSAPL	44.0	79.8
MOR	73.4	130.6
MCS	44.8	68.0

Note: MOE = modulus of elasticity, FSAPL = fiber stress at proportional limit, MOR = modulus of rupture, MCS = maximum crushing strength.

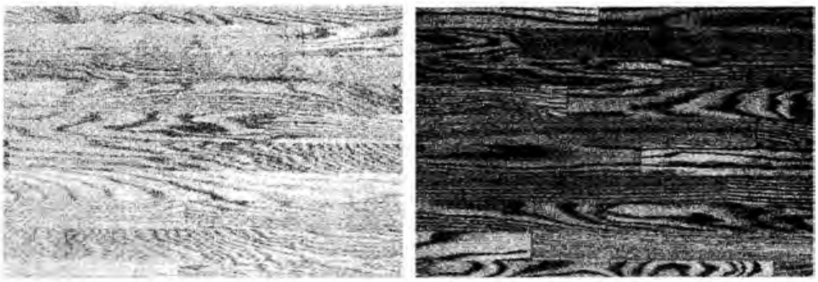


FIGURE 16.6 Various dyes can be added to change the color of the impregnated wood.

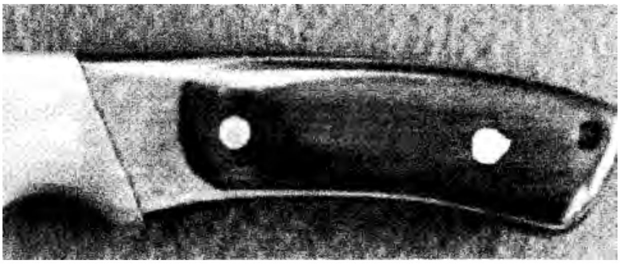


FIGURE 16.7 Knife handle made from acrylic impregnated veneers.

16.6 APPLICATIONS

The major uses of WPCs are for flooring, sports equipment, musical instruments, and furniture (Fuller et al. 1997). Flooring has the largest volume that includes solid plank flooring, top veneers of laminated flooring, and fillets for parquet flooring. As for sports equipment, patents have been issued for golf club heads (Katsurada and Kurahashi 1985), baseball bats, hockey sticks (Yamaguchi 1982), and parts of laminated skis. WPCs are used for wind instruments, mouthpieces of flutes and trumpets, and finger boards of stringed instruments (Knotik and Proksch 1971; Knotik et al. 1971). One area with potential is the use of veneer laminates for furniture, such as desk writing surfaces and tabletops (Maine 1971; Kakehi et al. 1985). A history of the commercialization of WPCs and future opportunities is covered by Schneider and Witt (2004).

16.7 POLYMER IMPREGNATION

Wood polymer composites are usually formed by impregnating the wood with a monomer which is polymerized *in situ* mainly in the lumen. Because the monomers are small, almost complete penetration of chemical is achieved. However, it is possible to impregnate wood with oligomers or polymers, however, penetration depends on the size of the oligomer or polymer. Chemical retention is often limited by the inability of the large polymers to penetrate into the wood structure. Several resin systems have been used to treat wood to improve performance properties. Figure 16.8 shows a very simple diagram of treating wood with a monomer.

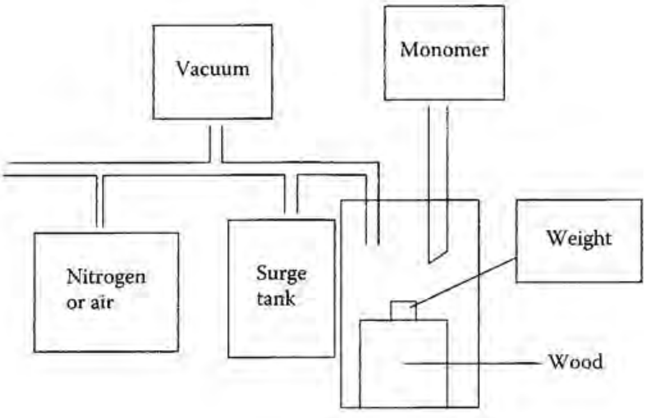


FIGURE 16.8 Simple system for the impregnation of wood with monomers.

16.7.1 EPOXY RESINS

Epoxy resin is a partially polymerized, clear solution, with a consistency slightly thicker than varnish at room temperature (21°C). Just before treating wood, the epoxy resin is mixed with hardener. It is cured or hardened within the lumen structure from a few minutes to a few hours depending upon the hardener and temperature. Treatment with epoxy resin is usually performed on veneers because of its large molecular size and high viscosity which does not allow for deep penetration into larger specimens. Veneers are either vacuum treated or soaked in the epoxy resin-hardener solution and then cured. Mechanical properties are greatly increased with epoxy resin treatments, especially hardness (Rowell and Konkol 1987). Epoxy resins are used for wooden boat hulls, the outer ply of plywood, and strengthening softened or decayed wood.

16.7.2 COMPRESSION OF WOOD WHILE HEATING AND CURING WITH RESIN

Wood can be compressed using heat either with or without resin that improves strength, stiffness, and stability.

16.7.2.1 Staypak

Compressed wood containing no resin is called Staypak (Seborg et al. 1945). During compression with 1400–1600 lb/in^2 pressure, with temperatures of 170–177°C, lignin will flow relieving internal stresses, but also causing a darkening of the wood. The compression time varies with the thickness of the wood, but usually to a specific gravity of at least 1.3 (Rowell and Konkol 1987). The resultant wood product has a slower moisture absorption and hence a reduction in swelling. It is more dimensionally stable, but not necessarily more biological resistant. Tensile strength (both parallel and perpendicular to the grain), modulus of rupture, elasticity in bending, and impact bending strength of the wood are increased. Staypak is used for tool handles, mallet heads, and various tooling jigs and dies.

16.7.2.2 Compreg

Compreg is resin-treated, compressed wood, and made with layers of treated veneers (Stamm and Seborg 1951). The most common resin is phenol–formaldehyde. The veneers are treated to 25–30% weight gain based on oven-dried weight. The veneers are dried at 30°C or less to prevent the resin from curing. The resin is cured during the heating (140–150°C) and compression process (pressures of 1000–1200 lb/in^2). Water absorption is greatly reduced; biological resistance to decay, termite, and marine borer is increased; electrical, acid, and fire resistance are increased. Strength properties of Compreg are increased, except for impact bending strength. The abrasion resistance and hardness are also increased compared to untreated wood. Compreg has many uses from knife handles and tools to musical instruments (Rowell and Konkol 1987). Figure 16.9 shows a clarinet made by AI Stamm from compreg in the 1950s.

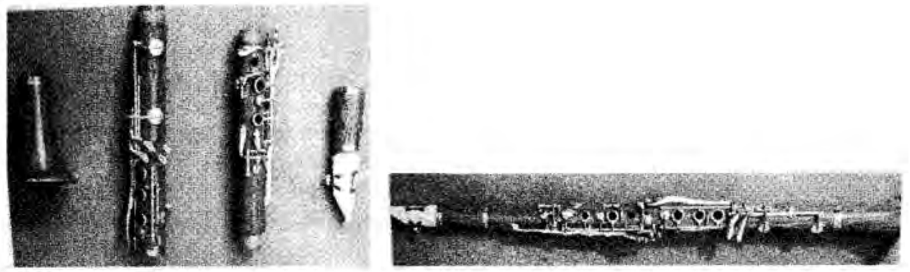


FIGURE 16.9 Compreg clarinet made by A1 Stamm.

To show that the instrument could be used even when wet, the clarinet was placed in a fish tank with fish the night before it was to be demonstrated. The next morning the clarinet was fine but the fish were dead probably from a small amount of phenol that may have leached from the instrument.

16.7.2.3 Staybwood

Staybwood is one product that is made by heating wood in a vacuum at high temperatures (93–160°C) in a bath of molten metal (Stamm et al. 1960). The high temperature causes the lignin to flow and the hemicelluloses to decompose, producing water-insoluble polymers. The process increases dimensional stability, but decreases strength and therefore has not been used commercially (Rowel1 and Konkol 1987).

16.8 WATER-SOLUBLE POLYMERS AND SYNTHETIC RESINS

Wood can be impregnated with water-soluble treatments such as PEG or resins (Impreg) that become insoluble after curing. Keeping the wood in a partially or completely swollen state increases dimensional stability, as well as strength and water repellency.

16.8.1 POLYETHYLENE GLYCOL

Polyethylene glycol (PEG) is a chemical with the following structure:

$$\mathrm{HO{-}CH_2CH_2{-}O{-}CH_2CH_2{-}(O{-}CH_2CH_2)_n{-}O{-}CH_2CH_2{-}OH}$$

PEG 1000 is most commonly used when treating wood, usually undried, green wood (Mitchell 1972). It is a waxy, white solid that has an n value (average molecular weight) of 1000 and it can penetrate the cell wall because of its small size. It melts at 40°C, readily dissolves in warm water, is noncorrosive, odorless, and colorless, and has a very high fire point (305°C) (Rowel1 and Konkol 1987). Molecular weights up to 6000 are soluble in water.

To treat wood with PEG 1000, the wood is placed in a container and covered with a 30–50 wt.% solution dissolved in water. The treatment is based on diffusion and therefore soak time will vary depending upon the thickness of the specimen. PEG remains in the cell walls when the wood is dried because of its low vapor pressure. The rate of diffusion into the cell wall increases as water evaporates from the solution (Stamm 1964).

Treatment temperature is usually from 21°C to 60°C, but diffusion can be accelerated with increasing the temperature and/or the concentration of the solution. After treatment, the wood is air dried in a ventilated room. The drying time also depends upon specimen size.

PEG is not chemically attached to the wood, and because it is water soluble, it will leach out if it gets wet (see Chapter 4). Glycol attracts moisture, so if the relative humidity reaches above 70%, the wood becomes sticky.

PEG has many uses especially in prevention or reduction of cracking due to drying sound wood for tabletops, to partially decomposed wooden artifacts, or archeological waterlogged wood.

16.8.2 IMPREC

Impreg is wood that has been treated with a thermosetting, fiber-penetrating resin and is cured without compression (Stamm and Seborg 1962). Phenol–formaldehyde resin-forming systems with low molecular weights are the most successful thermosetting agents. The resins penetrate the cell wall (25–25% weight gain) and keep the wood in a swollen state, dried at 80–93°C for 30 min, and then are polymerized by heat (155°C for 30 min) to form a water-insoluble resin in the cell wall (Rowell and Konkol 1987). Treatments are usually done on thin veneers (<9 mm thick) due to time.

The cured product is usually reddish brown with reduced swelling, shrinkage, grain raising, and surface checking. It improves the compression strength, but reduces the impact bending strength. Impreg shows resistance to decay, termite, and marine-borer attack, and it has a high resistance to acid. It is suited for pattern and die models as well as electrical control equipment.

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